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Towards single-molecule optoelectronic devices

Lijue Chen^{1†}, Anni Feng^{1†}, Maoning Wang^{2,3†}, Junyang Liu¹, Wenjing Hong^{1*}, Xuefeng Guo^{3*} & Dong Xiang^{2*}

¹State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Collaborative Innovation Center of Chemistry for Energy Materials, Xiamen University, Xiamen 361005, China;

²Tianjin Key Laboratory of Optoelectronic Sensor and Sensing Network Technology, Institute of Modern Optics, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300071, China;

³Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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Benefiting from the development of molecular electronics and molecular plasmonics, the interplay of light and electronic transport in molecular junctions has attracted growing interest among researchers in both fields, leading to a new research direction of "single-molecule optoelectronics". Here, we review the latest developments of photo-modulated charge transport, electroluminescence and Raman spectroscopy from single-molecule junctions, and suggest future directions for single-molecule optoelectronics.

molecular electronics, molecular optoelectronics, single-molecule junction

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1 Introduction

Since Feynman [1] delivered his famous speech of "Plenty of Room at the Bottom", the design of materials or devices from nanomaterials, single molecules, or atoms and the manipulation of nanoscale objects have aroused great interest in scientific communities, and many nanoscale technologies are now emerging. Nanoscale matters such as molecules, nanoclusters and quantum dots exhibit novel quantum properties such as quantized conductance [2], quantum interference [3], and Coulomb blockade [4], which have never been discovered on macroscopic scales. The newly discovered quantum effects of nanoscale systems can be exploited in novel multifunctional devices. Molecular electronics is an emerging nanotechnology inspired by Feynman's speech, which focuses on devices with single-molecule junctions and the charge transport through those junctions. Beyond conduction measurements of single-molecule devices, researchers have explored the interaction of electronic transport and light in single-molecule junctions, leading to a crossover field of molecular electronics and molecular plasmonics, and an emerging field of "single-molecule optoelectronics" [5–8]. Molecular electronics explores the charge transport through molecular junctions and the building of functional electronic devices with single-molecule junctions [9,10], while molecular plasmonics stimulated by photo illumination or an electric field are widely used in plasmonic devices and molecular spectroscopy studies [11,12].

[†]These authors contributed equally to this work.

^{*}Corresponding authors (email: whong@xmu.edu.cn; guoxf@pku.edu.cn; xiangdongde@nankai.edu.cn)

When single-molecule junctions are illuminated by light, the electrons excited by the light-induced plasmons can be conducted into single-molecule junctions, where they are detected as photocurrent. Meanwhile, the recombination of electrons and holes releases photons that are detected as light emission signals [13–15]. Under an applied bias, the electrons undergo inelastic tunneling or radiative transition, creating photons that can be detected by spectroscopic techniques [16,17]. Thus, plasmons initiate electron-photon conversion and form a bridge between molecular electronics and molecular plasmonics. Because of quantum size effects, single-molecule devices possess more properties than conventional devices. Single-molecule devices provide quantum models for molecular plasmonics, which can be implemented in conventional optoelectronic devices [18]. Moreover, owing to their plasmonic properties, single-molecule devices can overcome the limited transportation speed and functionality of conventional electronic devices. Versatile and ultrafast single-molecule optoelectronic devices are essential for future information techniques such as quantum computing and quantum communication [19]. Towards realizing single-molecule optoelectronics, many novel photoresponsive molecular junctions with interesting physical effects, such as photo/plasmon-assisted tunneling and orbital control of photocurrent, have been designed, fabricated, and observed [20–22]. The development of single-molecule optoelectronic devices would assist our understanding of the optoelectronic properties of single molecules. Such devices would also benefit other fundamental sciences, such as chemical reactions at the single-molecule scale, singlemolecule photo-electrochemistry, single-molecule biophysics, next-generation DNA sequencing, and molecular computing [23–26].

In this review, we describe three recent advances in singlemolecule optoelectronics: light-induced modulation of charge transport at molecular junctions, bias-induced photon emission from molecular junctions, and the optical spectroscopic characterization of current-carrying molecular junctions.

2 Photo-modulated charge transport

The interaction of light with molecular junctions is attracting growing interest. On the one hand, it poses challenging experimental and theoretical problems; on the other hand, it is potentially applicable as a characterization and control tool. The topic stands at the interface between two important research fields, molecular electronics and molecular plasmonics. This section focuses on photo-modulated charge transport. We begin with hot electron creation and transport in bare plasmonic nanogaps, then move to photo-modulated charge transport in molecular junctions.

2.1 Photovoltages and hot electrons in nanogaps

The structures with nanoscale gaps can host confined plasmon, the excitation of which can produce an extremely large local electric field. The local electric field in the nanogap can exceed the amplitude of an incident wave by several orders of magnitude. This enhanced electric field enables surface photochemical processes and may involve "hot" electrons, *i.e.*, gas-phase electrons that are excited by photons or by decay of plasmon excitations. On femtosecond time scales, hot electrons are not thermally equilibrated with the electron gas and their energy considerably exceeds the energy distribution of thermal carriers. When light illuminates a plasmonic nanogap configured for electronic transport measurements, several processes become possible, such as thermal expansion, photon-assisted tunneling, rectification, photothermoelectric response, photoemission, and hot electron photocurrent.

Figure 1 illustrates the possible processes in a light-illuminated bare nanogap. Thermal expansion occurs when optical absorption locally increases the temperature of the metal electrodes, increasing the nanogap size and hence changing the current-voltage characteristics (dI/dV) in the tunneling regime (Figure 1(a)). However, this process cannot produce a zero-bias photocurrent or an open-circuit photovoltage. In photon-assisted tunneling, the incident optical field induces a time-varying voltage $V_{\rm opt}$ at the optical frequency across the nanogap. The optical field is excited by radiation of energy $\hbar\omega$, enabling processes that change the electron's energy. According to the Tien-Gordon approach [28], the radiation energy probably influences the tunneling probability between the two electrodes, allowing tunneling processes that are otherwise prohibited (Figure 1(d)). Tunneling is mediated by screening/work function effects and the energy-dependent density of states of the metal electrodes. The result is a bias-dependent current $I_{\rm ph}$ that linearly depends on the intensity of the incident radiation. The current can be nonzero at zero bias if the energy-dependent tunneling between the electrodes is asymmetric on a scale of $\hbar\omega$. If the tunneling nonlinearity is sufficiently small (on a bias scale of $\hbar\omega/e$, the photon-assisted tunneling becomes equivalent to classical rectification (Figure 1(b)). Depending on the energy of the incident photons and the effective work function of the metal electrodes, the electron may escape from the metal surface. This process is called photoemission. When a photoelectron acquires the appropriate momentum direction to reach the other electrode and there is a net imbalance in the photoemissions of the two electrodes, a photocurrent can be generated in the absence of an applied bias (Figure 1(c)). Moreover, light illumination can imbalance the temperature across the junction. The ensuing temperature change ΔT induces a photothermoelectric effect on the junction conductance, creating a thermo-voltage and hence

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Figure 1 Photo-activated processes in nanoscale junctions without molecules. (a) Thermal expansion due to light-induced heating reduces the effective tunnel barrier between the source and drain electrodes; (b) optical rectification in the case of nonlinear current-voltage characteristics of a nanoscale junction; (c) a photo-emitted electron acquires sufficient energy from the light field to tunnel to the opposite electrode; (d) photon-assisted tunneling: an electron obtains sufficient energy from the optical field to tunnel into an empty state; (e) photothermoelectric current driven by optical heating that warms the electronic distribution more on one electrode than the other; (f) hot-electron photocurrent generated by the small population of electrons at energies comparable to $\hbar\omega$ that tunnel before equilibrating with the bulk of the electron gas. Reproduced with permission from Ref. [27], copyright 2018, SPIE (color online).

an additional tunneling current I_{ph} [29]. Consequently, a photovoltage is generated in the open-circuit limit, as shown in Figure 1(e).

Hot electron photocurrent is similar to both internal photoemission and the photothermoelectric response, as shown in Figure 1(f). However, unlike internal photoemission, hot electrons may be produced through plasmon decay as well as by photo-absorption, and unlike the photothermoelectric response, they must tunnel before they have equilibrated with the bulk of the electron gas. A net short-circuit photocurrent at zero bias requires an imbalanced hot-electron production between both sides of the junction. A net shortcircuit hot electron current I_{he} would generate an open-circuit photovoltage at zero bias. If the hot electrons are mainly generated by plasmons, the photocurrent should depend on the polarization and wavelength of the plasmon excitations.

2.2 Photoconductance in molecular junctions under light illumination

Photoconductance (PC) occurs when the electronic conductance of a molecular junction changes under light illumination. Several PC mechanisms have been proposed and accepted [30,31]. The first mechanism is a photo-induced change of the molecular structure under light illumination [32–34]. The second mechanism is the opening of additional conduction channels following resonant optical transitions under light illumination, which arises from the inherent asymmetry at the junction [5,35]. The third mechanism is the opening of photo induced conduction sidebands in the single-electron transmission function. This mechanism is called adiabatic photo-assisted tunneling or the Tien-Gordon mechanism [36]. Finally, PC can result from exciton binding in molecular junctions [30]. These four mechanisms are detailed in the following sections.

Let us address the first mechanism, by which an illuminated molecule undergoes a structural change. The energy structures of flexible molecules such as azobenzene and diarylethene will be correspondingly changed under light illumination [7]. Thus, the conductance of a molecular junction may switch its behavior when illuminated by light of different frequencies. Among the most challenging barriers to fabricating stable and reproducible molecular switches is controlling the properties of the molecule-electrode interface. Previous studies have reported only one-way optoelectronic switching (from the insulating open form to the conducting closed form, or vice versa) in single diarylethenes or molecular monolayers sandwiched between electrodes [37,38]. This one-way response was attributed to quenching of the excited state in the presence of the electrode. Such quenching occurred through strong moleculeelectrode couplings produced by the covalent amide/sulfur linkages.

To overcome this problem, Jia *et al.* [33] incorporated three methylene (CH₂) groups into each side of the diarylethenes backbone. The CH₂ groups decreased the effective molecule-electrode coupling, enabling reversible photoswitched conductivity as shown in Figure 2. They demonstrated a fully reversible, single-molecule electrical switch with very high accuracy (on/off ratio of ~100), stability (over one year), and reproducibility (more than 100 photoswitching cycles). The successful construction of a fully reversible



Figure 2 Photo-induced changes in molecular structure. (a) Schematic of a graphene-diarylethene-graphene junction highlighting the molecular structures; (b) measured current-voltage (I-V) curves through a diarylethene molecule that reversibly switches between the closed and open forms when exposed to ultraviolet (UV) and visible (Vis) radiation, respectively; (c) measured current versus time under periodic exposure to UV and Vis radiation. Reproduced with permission from Ref. [33], copyright 2016, AAAS (color online).

single-molecule photoelectric switch with large on/off ratio paves the way for practical development of photoelectronic devices that exploit molecular electronic properties.

Small structural changes in a molecular junction can lead to significant variations in the single-molecule electronic properties of the junction, suggesting that reactions on the single-molecule level can be studied by monitoring the conductance changes at junctions. Huang et al. [34], explored whether the single-molecule break junction technique can detect photo-thermal reaction processes in a photochromic dihydroazulene/vinylheptafulvene system. Employing mechanically controllable junction technique, they measured the conductance of dihydroazulene/vinylheptafulvene under light illumination and heating. The conductance clearly altered during the molecular photo-thermal reaction process. By statistically analyzing the break junction data, one can probe the reaction kinetics and their reversibility, including any isomerization occurring during the reaction. Their study opens a window for tailoring the product ratios of chemical reactions in nano-structured environments such as molecular junctions.

The third main mechanism is photon-assisted tunneling [31,39]. Surface plasmon polaritons can be excited by photons when the momentum matching condition is satisfied. Vadai *et al.* [31] designed a new platform for investigating the photon-assisted tunneling mechanism that excites surface plasmons. As shown in Figure 3(a), the break junction consists of two 40 nm-thick gold electrodes on evaporated glass slides. The gap between the two slides, initially set to ~500 nm, can be mechanically controlled with high accuracy by bending or relaxing the top slide. Because the squeezable break junction is constructed from two Au-covered glass slides with sufficient roughness, one can measure single-atom contacts. Sufficient roughness is also essential for plasmon creation within the gap. In Ref. [31], plasmons within the gap were generated by attaching a glass prism to



Figure 3 A squeezable-molecule break junction setup for single-molecule conductance measurements. (a) Schematic of the experimental approach. When the prism is illuminated by a laser, free photons and surface plasmons are coupled and confined within the gap between the two electrodes. (b) Representative conductance traces recorded during the separation process without (black) and with (red) laser illumination. Reproduced with permission from Ref. [31], copyright 2013, American Chemical Society (color online).

the bottom slide. The plasmon resonance conditions were found by varying the angle θ of the p-polarized indident laser with respect to the surface normal. To detect θ , they monitored the intensity of the reflected light. The maximum plasmon coupling is evidenced by a sharp drop in the reflectivity. Typical conductance traces are presented in Figure 3(b). A single molecule was considerably more conductive under light illumination than in the dark.

The energy gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO energy gap; see Figure 3(b)) was >3 eV, exceeding the energy of the created plasmons (1.59 eV). Therefore, photon absorption by the molecules within the junctions cannot source the enhanced conductance. Instead the conductance of the molecular junction may be influenced by the plasmonic oscillating field [31]. This interaction can be analyzed by the Tien-Gordon model, which considers the time-dependent modulation of the electronic energies [5]. The Tien-Gordon model treats the plasmon field as a potential V_{ω} across the nanoscale gap, which oscillates at the plasmon frequency ω . An electron tunneling through the junction with initial energy E can either absorb or emit n photons with energy $\hbar\omega$, and hence finish the tunneling process with energy $E \pm n\hbar\omega$. In this way, one can change the transmission probability of an electron across a junction (which strongly depends on the electron energy) and the overall DC conductance of the junction. In other words, V_{ω} behaves as a gate that shifts the transmission probability of an electron across a junction.

Finally, let us discuss the fourth mechanism, photoconductance from exciton binding at molecular junctions. In a theoretical analysis and experimental verification, Zhou *et al.* [30] showed that photoconductance under light illumination can occur by Coulomb interactions between the electrons and holes in the molecular bridge, which changes the conductance. They used an NH_2 -PTCDI- NH_2 molecule, which is perfectly symmetric and undergoes no structural changes under light illuminations. The experiments were

performed on scanning tunneling microscopy break junctions (STM-BJs) with perylene tetracarboxylic diimide (PTCDI) molecules attached to gold electrodes via Auamine bonds (Figure 4(a)). Using a monochromator, they applied photon emissions of fixed wavelength (~495 nm, corresponding to an energy of 2.5 eV), in resonance with the HOMO-LUMO gap of PTCDI. The photons illuminated the molecular junction in toluene solution through an ultrathin (~600 µm-diameter) optical fiber cable. The conductance traces recorded in the electrode separation process are shown in Figure 4(b). The gray curves (measured in the dark) plateaued at a lower level than the blue curves (measured under illumination). Figure 4(c) is a conductance histogram generated from more than 1000 conductance traces. The PC effect is clearly visible; the non-illuminated conductance peaks are centered around $G_{\text{dark}} \approx 1.25 \times 10^{-5} G_0$, whereas the illuminated ones are centered around $G_{\text{light}} \approx 1.75 \times 10^{-5} G_0$, higher than in the dark. As the molecule is perfectly symmetric and does not structurally change under light illuminations, Zhou et al. [30] proposed a new mechanism to explain their observations. Considering the simplest model of transport through a molecular junction, namely, the coupling of the HOMO and LUMO to the gold electrodes (Figure 4(b, d)), they assumed that the electrodes' Fermi level was closer to the HOMO than the LOMO. In this case, the conductance is dominated by hole tunneling through the HOMO. Under dark conditions, the conductance exponentially decayed with increasing energy gap between the HOMO and the electrodes' Fermi level. When illuminated with light near the resonant frequency of the HOMO-LOMO gap, the electrons were likely excited from the HOMO to the LUMO. A hole tunneling from the electrode to the HOMO was then attracted to the charge in the LOMO through the Coulomb interaction. Consequently, the HOMO energy was pushed toward the Fermi level, reducing the tunneling barrier and increasing the conductance.

2.3 Plasmon-induced chemical reactions

Plasmon-induced chemical reactions of molecules adsorbed to metal nanostructures are attracting increasing attention as photocatalysts that can form or dissociate chemical bonds [13], further modulating electron transport. These reactions can be invoked by an indirect hot-electron transfer mechanism that generates electron-hole pairs in the metal nanostructures by nonradiative decay of the localized surface plasmons (LSPs). The hot electrons then transfer to form a transient negative ion (TNI) state of the adsorbed molecule (Figure 5(a)) [13]. The plasmons can also dissociate the molecules through vibrational excitation after the transfer of the TNI states generated by the hot electrons [41].

Figure 5(b) illustrates the direct intramolecular excitation mechanism proposed by Kazuma *et al.* [40]. STM observa-



Figure 4 Mechanism of enhanced conductance under light illumination. (a) Schematic of the measurement strategy. An NH₂–PTCDI–NH₂ molecule bridging two electrodes is illuminated with laser light. (b) Under dark conditions, the current is dominated by hole-transport through the HOMO. (c) Conductance histograms under dark (gray) and illuminated (blue) conditions, generated from more than 1000 curves. Representative curves are presented in the left panel. (d) Illumination excites the electron to the LUMO, which becomes partially filled. Consequently, a hole entering the HOMO is attracted to it, causing an effective shift of the HOMO level towards the Fermi level, accompanied by enhanced conductance. Reproduced with permission from Ref. [30], copyright 2018, American Chemical Society (color online).

tions clearly revealed that when excited by LSP, the molecules near the tip position transformed into two identical ball-shaped protrusions (Figure 5(d, e)). The dissociated chemical species exhibited the same appearance as CH_3S molecules obtained by injecting tunneling electrons into a $(CH_3S)_2$ molecule. Based on this STM study and theoretical calculations, they concluded that their plasmon-induced chemical reaction occurred by a direct intramolecular excitation mechanism.

The chemical enhancement effects in surface-enhanced Raman spectroscopy (SERS) induced by localized surface plasmons have been explained by charge transfer from metals to molecules (Figure 5(c)) [42]. The Raman intensities of pyridine molecules adsorbed on coinage metals such as Ag, Cu, and Au were enhanced by electron transfer from the highest occupied state of the metal near the Fermi energy E_F to the unoccupied molecular orbitals. Similarly to the mechanism of enhanced Raman scattering, (CH₃S)₂ molecules on Ag(111) were rotated and dissociated when vibrationally excited by inelastically tunneled electrons. The dissociation occurred through vibrational excitation of the C–H stretch mode.

In summary, molecular junctions are complex systems that cannot be fully captured by theoretical models of opticalelectrical behaviors in bias junctions, which are often simplified to tackle the target problem. Despite these experimental and theoretical difficulties, this field has remarkably progressed throughout the past decade. The growing availability of reliable nanogaps that can combine optical and electrical probes suggests that molecular optoelectronics on

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Figure 5 Three excitation mechanisms of plasmon-induced chemical reactions. (a) Indirect hot-electron transfer mechanism. Hot electrons generated by nonradiative decay of a localized surface plasmon are transferred, forming transient negative ion states of the molecule. (b) Direct intramolecular excitation mechanism. The localized surface plasmon induces direct excitation from the occupied state to the unoccupied state of the adsorbate. (c) Charge transfer mechanism. The electrons are resonantly transferred from the metal electrode to the molecule. (e) Schematic of the experiment for real-space investigation of the plasmon-induced chemical reaction in the nanogap between the silver tip and a metal substrate. Topographic STM images of $(CH_3S)_2$ molecules on the silver surface (d) before and (f) after irradiation with *p*-polarized light. Reproduced with permission from Ref. [40], copyright 2018, AAAS (color online).

the nanoscale will be developed in the near future [5].

3 Single-molecule electroluminescence

By probing the light emission from bias-driven single molecules, we can begin to understand the mechanism of electron-to-photon conversion. Moreover, understanding and manipulating the electroluminescence from single molecules is vital to the development of single-molecule light-emitting diodes (LEDs), molecular-scale optoelectronic logic gates, and ultrafast electronic-plasmonic devices for molecular optoelectronics [43,44]. Various single emitting units such as metal clusters, quantum dots, and molecules have been investigated by STM-induced light emission [45–49]. Nevertheless, the experimental investigation of electroluminescence from single-molecule junctions remains a major challenge.

When a molecular emitter is hybridized with a metal electrode, its emission is quenched. Such quenching hinders the integration of single-molecule emitters into electronicplasmonic circuits. Marquardt *et al.* [50] synthesized a rodlike molecule consisting of a central 2,6-dibenzylamino coresubstituted naphthalenediimide (NDI) chromophore, two long oligo-(phenylene ethynylene) (OPE) rods, and phenanthrene anchor units (Figure 6(a)). They built a nanotubemolecule-nanotube device with an electroluminescence property in solution at room temperature. The device was formed by inserting the molecule into the gap between two free-standing carbon nanotube electrodes, forming a bridge between the electrodes. The device, called an NT-M-NT device, was fabricated as shown in Figure 6(b–e). The light emitter was the NDI core, which emits strong red fluorescence, and the two long OPE rods minimized the quenching caused by coupling the electrodes to the light emitter. The rods also improved the solubility of the molecule and enhanced its electrostatic interaction with the carbon nanotube electrodes. The phenanthrene anchors interacted with the carbon nanotube electrodes by van der Waals interactions. The stability of the NT-M-NT device was confirmed by current-voltage characterization. Electroluminescence only occurred when the voltage bias between the two nanotubes exceeded 4 V. Therefore, by controlling the bias, the electroluminescence of the molecule can be switched on and off. The collected electroluminescence spectrum of an NT-M-NT junction (Figure 6(f)) coincided with the fluorescence spectrum of the rod-like molecules on highly ordered pyrolytic graphite. Marquardt et al. reported the first roomtemperature electroluminescence from single-molecule junctions. However, the electroluminescence efficiency (one photon per 10⁹ electrons) was extremely low. The low electron-to-photon conversion efficiency and the broad band of the electroluminescence spectrum limit the applicability of this device.

Schull *et al.* [51] constructed a single-molecule LED by bridging the metal surface and the tip of a low-temperature STM with a polythiophene molecular wire. The molecular wire suspended between the two electrodes can be manipulated by changing the tip-sample distance or the applied bias. The maximum light emission efficiency of their singlemolecule LED was of the order of 10^{-5} photons/electrons, four magnitudes higher than that of Marquardt *et al.*'s NT-M-NT device. Using the same setup, Schull's group [52] then reported a narrow line emission from a porphyrin wired by terthiophene. The porphyrin molecule acted as an electrically driven molecular emitter, and the terthiophene groups



Figure 6 (a) Structure of the rod-like molecule in Ref. [50]. (b–e) Fabrication of the NT-M-NT device. (b) A freestanding metallic nanotube (black bar) was fabricated on a palladium electrode (grey) by dielectrophoresis; (c) the nanotube was disintegrated by electrical burning, forming a gap; (d) the NT-M-NT junction was constructed by dielectrophoretic deposition of molecules from solution into the gap; (e) the molecule emitted light under a voltage bias of V. (f) The electroluminescence spectrum of the NT-M-NT device (open red circles) closely resembles the fluorescence spectrum of molecules on highly oriented pyrolytic graphite (black line). Reproduced with permission from Ref. [50], copyright 2010, Nature Publishing Group (color online).

worked as spacers to avoid the hybridization of porphyrin to the metal electrodes. The shape of the emission band could be tuned by varying the distance between the emitter and the substrate, and the light emission intensity could be controlled by adjusting the applied voltage. Recently, they found that a single graphene nanoribbon junction emits a bright narrow line of red light, whose width can be controlled by tuning the applied bias and the tip-sample distance [53]. Molecular emitters can now be wired into electrical circuitry, and the next challenge is to fabricate stable and highly efficient molecular devices.

Du *et al.* [54] attempted the construction of molecular optoelectronic devices from molecular monolayers. Their integrated molecular electrically driven plasmon sources consisted of two metallic electrodes connected by self-assembled monolayers (SAMs) as tunneling junctions (Figure 7(a)). The molecular junctions were assembled on gold substrate as the bottom electrode, and the top electrode was a liquid alloy of eutectic gallium and indium (EGaIn). The gold substrate was sufficiently thin for the detection of electrically created surface plasmon polaritons (SPPs) and

LSPs. To study the influence of symmetrical and asymmetric tunneling barriers, they designed two kinds of molecules, S(CH₂)_{n-1}CH₃ (SC_n, n=10, 12, 14, 16 and 18) and (4-((4-(ferrocenyl)-phenyl)ethynyl)phenyl)methanethiol (S-OPE-Fc) (Figure 7(b)). The HOMO-LUMO gaps of the SC_n junctions ranged from 8 to 9 eV, and the Fermi levels of the bottom and top electrodes were both close to -4.2 eV, approximately half the energy of the HOMO-LUMO gaps of SC_n . Therefore, devices installed with the SC_n junctions exhibited symmetric tunneling current, and could be tuned by the *n*-dependent tunneling decay coefficient. Meanwhile, devices installed with the S-OPE-Fc junctions showed asymmetric charge transport phenomena and behaved as molecular diodes. Under positive bias, the HOMO level of the S-OPE-Fc junctions shifted to below the Fermi levels of both electrodes, and the charge transport was dominated by direct tunneling. However, under negative bias, the HOMO level located between the Fermi levels of the two electrodes and the tunneling behavior changed from direct to sequential. The plasmonic properties of the devices based on the SC_{12} SAMs were then characterized, confirming excitation of the SPPs and LSPs. The SPPs were excited at the edges of the molecular junctions and propagated along the Au-SAM-air and Au-SAM-PDMS interfaces, whereas the LSPs were excited around the SAM-based tunneling junctions (STJs). The emission inhomogeneity in the STJs also confirmed an effective electrical-contact area of the Au-SAM-EGaIn junction. The wavevector of the SPPs from the 50 nm-thick Au bottom electrodes was further investigated, and the spectra of the STJ-excited plasmon sources were collected at different biases. The spectra were increasingly blueshifted at higher negative biases (Figure 7(c)). Next, the polarization of the plasmon sources was examined on defocused images of the SC12 and SC16 SAMs on the Au substrates. The different dipole orientations in the two plasmon sources suggested that the SAMs were polarized by through-bond tunneling, controlled by the molecular structures of the SAMs. The plasmon source based on the S-OPE-Fc SAMs, which behaved like molecular diodes, exhibited negative-positive voltage switching (Figure 7(d)). Therefore, the properties (polarization orientation and plasmon frequency) of this optoelectronic device can be controlled at the molecular scale by tuning the SAM structure and the applied bias. This work is an important step toward the development of molecular optoelectronics, and presents a new strategy for integrating molecular junctions into functional devices. In the future, optoelectronic devices fabricated with STJs can be downscaled to single-molecule optoelectronic devices without requiring external light sources and optical antennas.

Although STJs are a promising developmental strategy for electrically driven LEDs, future STJ-based devices should be downscaled to single-molecule sizes. At present, most of the single-molecule LEDs are restricted to ultrahigh vacuum



Figure 7 (a) On-chip electrically driven plasmon source in Ref. [54]; (b) Au-SAM-EGaIn based on SC_n and O-PE-Fc junctions; (c) bias-dependent electroluminescence spectra of SC_{12} SAM on 50 nm-thick Au substrate; (d) negative-positive voltage switching of S-OPE-Fc SAM. Reproduced with permission from Ref. [54], copyright 2016, Nature Publishing Group (color online).

operation at low temperature, because the fluorescence of a single-molecule emitter is easily quenched. A single-molecule LED running at ambient environment remains to be developed. The compressive mechanism of single-molecule electroluminescence [55] and the working conditions of future single-molecule LEDs could be clarified by other characterization techniques such as noise spectroscopy.

4 Raman spectroscopy of molecular junctions

In situ configuration characterization clarifies the relationship between the structure and electronic behavior of singlemolecule junctions. Characterizing techniques for singlemolecule junctions include inelastic electron tunneling spectroscopy, short noise spectroscopy and optical spectroscopy [5,7,56]. Optical spectroscopy acquires the dynamic fingerprint information of molecules in real-time under ambient conditions. However, obtaining the optical signals of molecular junctions is difficult because of mismatch between the optical diffraction limits and the length scales of molecules [6]. Molecular junctions have been characterized by optical techniques such as Raman spectroscopy, UV-Vis absorption spectroscopy. Fourier transform infrared spectroscopy, and X-ray spectroscopy [57-60]. Among these techniques, Raman spectroscopy most reliably extracts the fingerprints of single-molecule junctions. Aided by laserinduced surface plasmon resonance (SPR), the excitation light of Raman spectroscopy can be injected into the nanogaps between the electrodes. Moreover, Raman scattering is strongly enhanced by the SPR-generated electromagnetic field. This property is exploited in plasmon-enhanced Raman spectroscopy (PERS) [61], which has enabled single-molecule sensitivity of techniques such as SERS, tip-enhanced Raman spectroscopy (TERS) and shell-isolated nanoparticle enhanced Raman spectroscopy. With these techniques, we

can acquire the real-time fingerprint information of singlemolecule junctions [61-63]. Raman signals are enhanced by sharp metal nanostructures and specific wavelengths of the illuminating light. Under illumination, the Raman signals of the atomically sharp electrodes used to construct singlemolecule junctions are extremely enhanced inside the nanogap, realizing single-molecule SERS sensitivity at the molecular junction [20]. Thus, a hybridized electrical-spectroscopic technique for characterizing current-carrying junctions can feasibly be developed using Raman spectroscopy. This section discusses the development of optical characterization of molecular junctions by Raman spectroscopy. The discussion includes the methodology development of SERS from single-molecule junctions, and the physical and chemical phenomena of single-molecule junctions revealed by SERS investigations

4.1 SERS detection from single-molecule junctions

To obtain the desirable electromagnetic enhancement of SERS signatures inside a nanogap, subwavelength metal nanoparticles can be added on a common SERS platform. However, as this approach cannot precisely and flexibly control the gap width *in situ*, the single-molecule SERS contains uncertainty. Specific nanogaps can be controlled with high reproducibility by breaking-junction techniques. Therefore, breaking-junction techniques combined with Raman spectroscopy can acquire highly reproducible Raman signals. Herein, we introduce three main hybridized electric-spectroscopic techniques that precisely tune the *in situ* distance of nanogaps for detecting molecular junctions.

The combination of SERS with a mechanically controllable break junction (MCBJ) was pioneered by Tian et al. [64], who were interested in the SERS properties of molecular junctions at room temperature. Their hybridized system is schematized in Figure 8(a). The MCBJ is widely used for generating nanogaps of single-molecule junctions in molecular electronics research (for details, see Refs. [65,66]). Assisted by a piezoelectric transducer, the MCBJ setup enables precise control (sub-Å resolution) of the gap width between the fabricated pair of nanoelectrodes. 1.4-Benzenedithiol molecular junctions fabricated by MCBJ were characterized by the Raman signal from the nanogap between the nanoelectrodes [64]. The Raman signals from the molecular junctions were found to enhance with decreasing gap width (Figure 8(b)). This confirms that the Raman signal indeed originated from the electromagnetic field induced by the molecule in the gap, as the electromagnetic field between the nanoelectrodes strengthens when the gap is narrowed. Tian et al. [67] also investigated the polarization dependence between the Raman signal and incident laser. The Raman signal was largely enhanced when the incident laser was polarized parallel to the electrodes, and was dramatically



Figure 8 The first experiment of combined MCBJ and SERS. (a) Schematic of the MCBJ-SERS setup; (b) gap-width dependence of the SERS intensity at BDT molecular junctions. Reproduced with permission from Ref. [64], copyright 2006, American Chemical Society (color online).

suppressed by the perpendicular polarization. The enhancement when the laser polarization and nanogap directions were mismatched again corroborated that the enhanced Raman signals originated from the molecular junction inside the nanogap. Later, the vibrational spectroscopic and current-voltage (I-V) properties of nitro-substituted oligo(phenylene ethynylene) junctions were measured in the first simultaneous characterization of electrical and optical signals of molecular junctions.

Applying the electromigration method, Ward *et al.* [58] developed a nanogap-based substrate for single-molecule SERS measurements, and simultaneously measured the conductance and Raman signals from the molecular junctions in the fabricated nanogap. The electromigrated substrate consisted of two Au pads and an Au nanoconstriction (Figure 9(a)), and exhibited single-molecule SERS sensitivity [68]. The authors tested two types of molecules, pmercaptoaniline (pMA) and fluorinated oligophenylyne ethynylene (FOPE). The molecular junctions were bridged between pairs of nanoelectrodes. Simultaneously with conduction measurements, the Raman responses of the molecular junctions were recorded under 785-nm laser illumination. Unlike the above-described MCBJ technique, the gap width of the electromigration-fabricated electrodes was fixed, so devices with different gap widths exhibited different phenomena. Figure 9(b) displays the SERS mapping image of the vibrational mode of 1590 cm⁻¹, showing the signal emanating from the molecule junctions in the nanogap, and Figure 9(c) presents typical waterfall plots of the Raman time spectra and differential conductances of pMA. The strong correlations between the conductance and the Raman signal of the molecular junctions reflect the single-molecule sensitivity of the nanogaps. The fluctuations in the Raman intensity and spectral shifts were attributed to the movement or rearrangement of the single- or few-molecule junctions in the nanogaps, providing abundant information on the structure and dynamics of the molecular junction.

Liu *et al.* [69] developed a "fishing-mode" TERS method, which combines the "fishing-mode" STM-BJ with tip-enhanced Raman spectroscopy, and simultaneously collects the conductance and Raman measurements of single-molecule junctions. Figure 10(a) depicts the principle of "fishing-



Figure 9 (a) Au constriction with a nanogap fabricated by electromigration; (b) SERS mapping of pMA at the vibrational mode of 1590 cm^{-1} ; (c) time differential conductance and SERS spectra of a single or few pMA junctions. Reproduced with permission from Ref. [58], copyright 2008, American Chemical Society (color online).

mode" TERS. The STM tip moves toward the molecule adsorbed on the substrate, then grabs the targeted molecule to form a molecular junction in an electronic circuit. Whereas common STM-BJ techniques control the breakages of molecular junctions with a piezomotor, the molecular junctions in fishing-mode TERS break spontaneously under thermal or mechanical drift, and the tip traverses a small distance (0-3 Å) before fishing another molecule. The simultaneous conductance and Raman measurements revealed a positive correlation between the TERS spectra and conductance. Similar to Ward et al. [58], Liu et al. linked the fluctuations in the Raman spectra to single-molecule junctions. The molecular structure of single 4.4'-bipyridine molecular junctions was further investigated in bias-driven experiments, ranging the bias from 10 to 800 mV (Figure 10(b)). The v_{8a} Raman band of 4,4'-bipyridine depended on the bias voltage and was split in the nonlinear region of the *I-V* curve. To ascertain the origins of the bias-dependent Raman spectra, Liu et al. performed density functional theory (DFT) calculations of the vibrational modes in 4,4'-bipyridine-gold cluster models. The bias-driven Raman shifts were attributed to the variations in molecular structure and bonding strength. The DFT results are displayed in Figure 10(c). Increasing the bias increased the length of the Au-N bond between the pyridines



Figure 10 (a) Work principle of "fishing mode" TERS; (b) bias-dependent TERS spectra of the v_{8a} Raman band of 4,4'-bipyridine; (c) mechanism of applied-bias effect on the peak of the v_{8a} mode split. Reproduced with permission from Ref. [69], copyright 2011, Nature Publishing Group (color online).

and shortened the drain electrode. The enhanced strength of the Au–N bond eventually split the v_{8a} Raman band of 4,4'bipyridine. This innovative hybridized electro-optical technique is promising for studying the TERS of current-carrying junctions [70–73]. The ultrahigh spatial resolution of TERS can image single molecules [74], and might also realize the imaging of current-carrying junctions.

4.2 Physics inferred from the SERS of single-molecule junctions

The electronic structures and hence the vibrational modes of single-molecule junctions differ from those of free molecules. Consequently, recombinations of electronic structures and interactions at molecule-metal interfaces have revealed many previously unknown physical effects [75,76]. Electrical measurements at molecular junctions provide the electronic structure and the strength of a molecule-metal interaction, whereas the real-time fingerprints of the molecules adsorbed to the metal surface can be obtained by Raman spectroscopy [77].

4.2.1 Local heating at molecular junctions

Local heating is an unavoidable problem that influences the stability and performance of nanoscale electronic devices. Measuring the effective temperature in the current-carrying junctions, which is the joint effort of heating and heat dissipation, is essential for realizing a molecular device. Recent investigations have probed the effective temperature in molecular junctions by measuring the ratio of the Stokes and anti-Stokes components of the Raman scattering [78]:

$$\frac{I_{\rm v}^{\rm AS}}{I_{\rm v}^{\rm S}} = A_{\rm v} \frac{(w_{\rm L} + w_{\rm v})}{(w_{\rm L} - w_{\rm v})} \exp(-\hbar w_{\rm v} / k_{\rm B} T_{\rm v}^{\rm eff})$$
(1)

where I_v^{AS} and I_v^{S} are the intensities of the anti-Stokes and Stokes Raman signals, respectively, w_L and w_v are the frequencies of the incident laser and the Raman mode, respectively, A_v is the correction factor of the Stokes/anti-Stokes ratio, and T_v^{eff} is the effective temperature of a particular vibrational mode. Using this formula, one can extract the local temperature at a single-molecule junction from Raman spectroscopy data. Probing the thermal effects in biased molecular junctions is of great experimental and theoretical interest.

Ioffe et al. [79] published the first report of heating at single-molecule junctions derived from Raman spectroscopy data. They measured the Stokes and anti-Stokes Raman signatures at 4,4'-biphenyldithiol junctions fabricated by the "on-edge" method (Figure 11(a)). The effective temperature of the molecular junctions was then obtained from the intensity ratio of the Stokes and anti-Stokes signals. By relating the effective temperature to the applied bias, they observed the cooling and heating processes of two vibrational modes of the molecular junctions under 532-nm laser irradiation (Figure 11(b)). However, under 671-nm laser irradiation, the AS/S ratio was bias-independent (Figure 11(c)). Moreover, the temperatures of all vibrational modes at 0 V were very similar and approximated the actual temperature probed by a micro-fabricated gold/platinum thermocouple. The cooling and heating process occurred at different applied bias were attributed to the surface plasmon resonance mode and the hot electrons created by resonance. This new approach promises the exploration of heating in molecular junctions by hybridized electrical-optical techniques.

The estimation of effective temperature from the AS/S ratio at single-molecule junctions was theoretically validated by Galperin et al. [80,81]. In a pioneering study, they combined the nonequilibrium Green's function (NEGF), which has described single-molecule junctions in many studies, with common scattering theory of the Raman process, and hence investigated Raman scattering in a non-equilibrium junction system. Based on previous works, Ward et al. [78] detected the effective vibrational modes and electronic temperatures of biased amine-terminated oligophenylene vinylene (OPV3) junctions in the nanogaps between electromigrated gold electrodes pairs under vacuum conditions at 80 K. Their work, which was based on SERS, is more likely to detect the heating behavior in single- or few-molecule junctions than the above studies, because the behaviors of such junctions are reflected in the strong correlations between the conductance and Raman responses. Figure 12 plots the vibrational temperature and electronic heating measurements obtained in Ref. [78]. The effective temperatures of both vibration and electronic heating increased with the applied bias, consistent with the above-mentioned theoretical research. The asymmetry in the voltage-dependent effective temperature plots at different vibrational modes resembled the asymmetry in the *I-V* curve of this molecular junction device. This asymmetry was attributed to the different molecule-electrode coupling strengths at each side of the electrode pair. Thus, the effective temperature depended on the flow direction of the currents. The results of this work were also verified in a theoretical study by White et al. [82], who



Figure 11 (a) Experimental setup and differential conductances of "edgeon" junctions; (b) temperature (K) of the 1585 cm⁻¹ (black) and 1083 cm⁻¹ (red) modes versus the applied bias; (c) $T_{\rm eff}$ (V) of the 1585 cm⁻¹ (black), 1280 cm⁻¹ (blue), and 1083 cm⁻¹ (red) modes versus the applied bias. Reproduced with permission from Ref. [79], copyright 2008, Nature Publishing Group (color online).



Figure 12 (a) Effective vibrational temperatures of two OPV3 modes versus bias voltage: 1317 cm^{-1} (red) and 1625 cm^{-1} (blue); (b) effective temperature of electronic heating (blue) and dissipated electrical power (red) versus bias voltage. Reproduced with permission from Ref. [78], copyright 2011, Nature Publishing Group (color online).

probed the Raman scattering in molecular junctions by a pseudoparticle NEGF formulation, and thereby simulated the Raman scattering in a single OPV3 junction based on first principles. They showed that the Stokes line shifts to lower frequencies and broadens, as observed in previous experimental data.

Hybridized electrical-optical techniques can measure the local vibrational and electronic temperatures of singlemolecule junctions, offering a potential way to monitor the working conditions of such devices, or to evaluate and control the thermal effects in current-carrying junctions of future devices.

4.2.2 Molecular dynamics at single-molecule junctions

In situ characterization of the conformational and electronic structural changes of molecular junctions is essential for understanding their dynamics, and thereby capturing the multiple intermediate states during the break junction process [80,83]. Previous studies have reported strong correlations between conduction and the Raman responses of molecular junctions [58,69]. Complementary SERS can potentially acquire the real-time structures and configurations of molecular junctions.

Through simultaneous Raman and conductance measurements in an MCBJ-SERS system, Konishi et al. [84] monitored the thermal motions at single 4,4'-bipyridine junctions. Their junctions were formed by thermally induced selfbreaking of the nanofabricated MCBJ Au nanobridge. The dynamic process of the single-molecule junction was monitored by SERS. Figure 13(a) shows the conductance and evolutions of the SERS spectra during self-breaking of the Au nanobridge. Before the formation of the molecular junction and after its breakage (Region A and Region C respectively), the Raman signal was weak, indicating that its enhanced signal originated from single-molecule junctions. In Region B, the enhancement of the Raman spectra was synchronized with the plateau in the conductance versus time plot of the single-molecule junctions. Four bands of 4,4'bipyridine in the Raman spectrum of Region B were absent in the spectra of Region A and Region C, indicating their origin from the single 4,4'-bipyridine junction.

Repeated experiments revealed three main types of SERS spectra at the single 4,4'-bipyridine junction (Figure 13(b)). These three types of Raman spectra were assigned to the respective modes obtained in DFT calculations, namely, totally symmetric a modes, non-totally symmetric b_1 modes, and non-totally symmetric b_2 modes. The b_1 and b_2 modes were dramatically more intense than the *a* modes, indicating that the formation of the single-molecule junction strongly enhanced the two b modes, but did not influence the a mode. As the SERS signals of the b_1 and b_2 modes were related to the single-molecule junctions, these modes were further analyzed. Figure 13(c) shows the evolution of the Raman shifts of the ring breathing b_1 mode around 1050 cm⁻¹, and the corresponding conductance changes at the single 4,4'bipyridine junction. The time courses of the b_1 modes were consistent with the conductance fluctuations on the same time scale. The b_1 modes were highly conducting when the bridged molecule was perpendicular to the electrode plane. As the angle between the bridged molecule and the two Au electrodes increased, the strength of the molecule-electrode interaction decreased, with consequent energy increase of the molecule's vibrational modes.

The strong synchronization between the conductance and Raman shift reflects the dynamics in single-molecule junctions. These dynamics, and the precise configuration control



Figure 13 (a) Temporal changes in conductance and SERS spectra during self-breaking; (b) the three types of SERS spectra during the breaking process; (c) temporal changes in the conductance and Raman shifts around the b_1 mode. Reproduced with permission from Ref. [84], copyright 2012, American Chemical Society (color online).

of single-molecule junctions, are expected to be further investigated by hybridized electric-optical techniques.

4.3 Chemistry of single-molecule junctions inferred from SERS

The monitoring and further tuning of reactions at the singlemolecule level are significant for understanding the mechanisms of single-molecule chemistry. Molecular electronics techniques offer unique opportunities for monitoring and tuning molecular-scale chemical reactions, because electrical measurements are extremely sensitive to changes in molecular junction configurations and electronic structures, and also to the measuring environment [85]. Recently, electrical techniques have been applied in molecular-scale catalysis studies [86]. Moreover, in studies of single-molecule junction dynamics, electrical measurements have detected the transient states in the reactions [34,87]. Direct structural information of single-molecule junctions can also be obtained by Raman spectroscopy, which probes chemical reactions at molecular scales [88–90].

4.3.1 Bias-induced effects in molecular junctions

An electric field changes the electronic structure, vibrational mode energies, and coupling strength of a molecular junction. SERS efficiently probes an interfacial electric field in diffuse layers and reveals the bias-dependent vibrational modes of the molecules adsorbed on the metal surface. Therefore, SERS tools have been widely applied in spectroscopic electrochemistry [89]. However, exploring the bias-dependent SERS at single-molecule scales remains challenging. The single-molecule junction is a desirable model with potential for overcoming these challenges.

The bias-dependent TERS spectra of 4,4'-bipyridine reported by Liu et al. [69] (Figure 10(b)) provides rich information on the electronic structure and vibrational modes of current-carrying single-molecule junctions. They demonstrated a close relationship between the chemical bonding strength of the molecule-metal interface and the applied bias. Raman-spectroscopy probing of charge states in single-molecule junctions has been predicted in theoretical research [91]. Li et al. [92] reported the first experimental evidence of charging effects in single-molecule junctions. They fabricated gold– C_{60} –gold junctions by electromigration and obtained their bias-driven SERS spectra. The Raman spectra are displayed in Figure 14(a). Interestingly, as the applied bias V increased, the energy of many vibrational modes decreased as a function of V^2 . To understand the mechanism of the bias-driven phenomenon, the vibrational modes of the C_{60} and C_{60} anions in the bias regime -0.6 to 0.6 V were obtained in DFT calculations. Increasing the applied voltage increased the charge on C₆₀, causing blue shifts of the vibrational modes of the molecule. The shift of the $H_{g}(7)$ mode was negatively correlated with the bias-dependent charge of C₆₀ calculated by DFT, indicating that the bias-driven Raman shift was dominated by charging effects. The vibrational modes calculated by DFT matched the experimental data, suggesting that bias-induced charging effects caused the observed systematic mode softening.

Based on this work, Li *et al.* [93] then studied the biasdriven shifts in the vibrational modes of phenyl– C_{61} –butyric acid methyl ester (PCBM), an asymmetric derivative of fullerene. In contrast to the dominant quadratic shifts in the C_{60} junctions, the dominant shifts in the PCBM junctions were linear (Figure 14(b)). The linear phenomenon observed in PCBM was ascribed to contributions from vibrational Stark physics, which differ from the charging effects in C_{60} junctions. The vibrational Stark effects are useful for studying the dynamics and transient states of chemical reactions in single-molecule junctions [94].

The bias-induced structural changes of molecules can modulate optical signals and are potentially applicable to optoelectronic devices. Exploiting the Raman selection rules, Bi *et al.* [70] designed an electrically-driven molecular switch of 2,2',5',2"-tetramethylated *p*-terphenyl-4,4"-dithiol with two states: a Raman-active state and a Raman-inactive state. Under low applied bias, the two benzene rings of this junction were nonplanar with a dihedral angle of 92°, and the Raman signal was inactive. However, under high applied bias, the junction was transiently oxidized and the dihedral angle decreased to 50°, restoring the Raman activity. In this case, the Ramen activity was recovered by the extended π conjugation of the oxidized junction and the enhanced polarization. The electrically driven Raman activity in single-



Figure 14 (a) Bias-dependent Raman spectra of a representative C_{60} device. Reproduced with permission from Ref. [92], copyright 2014, National Academy of Sciences. (b) Bias-dependent Raman spectra of a PCBM device. Reproduced with permission from Ref. [93], copyright 2016, American Chemical Society (color online).

molecule junctions might enable the control of optoelectronic devices based on molecular junctions.

4.3.2 Probing chemical enhancement in single-molecule junctions

SERS signals are enhanced by two independent mechanisms: electromagnetic enhancement (EM) and chemical enhancement (CM), which are difficult to separate in common SERS experiments [95]. Chemical enhancement depends on the interaction between the adsorbed molecule and the surface metal. The molecule-metal interaction is evidenced by the charge-transport behavior between the two entities. Hybridized electric-optical techniques can wire molecules into circuits and measure their charge transport behaviors under irradiation. Thus, electric-optical techniques are ideal tools for investigating chemical enhancements of SERS signals [96,97].

The current-voltage characteristics contain much more information on the electronic structure, binding configuration and energy of the molecule-metal interface than conductance measurements [98,99]. Kaneko et al. [100] reported the site selection at single 1,4-benzenedithiol (BDT) junctions using a developed MCBJ-SERS system. They replaced the simultaneous conductance and SERS measurements in past studies by I-V measurements. BDT is widely studied as a model molecule in molecular electronics, but its conductance states are measured in multiple groups and remain controversial. Kaneko et al. [100] obtained three types of I-V curves at single BDT junctions. Figure 15(a) depicts the bidimensional I-V histogram accumulated from 203 I-V curves of single BDT junctions. After fitting the I-V curves to a single-level tunneling transport model, they obtained the statistical distribution of the coupling strength Γ of the molecule-metal interface. The obtained Γ s were separable into three states: the H state (0.14 eV), the M state (0.052 eV) and the L state (0.014 eV), each corresponding to a different



Figure 15 (a) *I-V* histogram overlaying the *I-V* curves of 203 singlemolecule BDT junctions; (b) statistical distribution of the coupling energy Γ ; (c) SERS spectra of single-molecule BDT junctions at different coupling energies where Γ increasing from bottom to top; (d) the plot is SERS intensity versus coupling energy, averaged from 96 v₁- and v₈-active samples. Reproduced with permission from Ref. [100], copyright 2016, American Chemical Society (color online).

configuration of the molecule-metal interface (Figure 15(b)). DFT calculations assigned the H, M and L coupling types to the bridge, hollow and top adsorption-site geometries, respectively. The SERS signal from the wired BDT was enhanced by both EM and CM mechanisms. The CM contribution to the SERS intensity was mainly affected by charge transfer resonances between the metal states and molecular electronic states. Consequently, the SERS intensities of the junctions increased with increasing Γ , implicating Γ as the main factor of CM (Figure 15(c)). Further analysis revealed a strong correlation between the coupling strength Γ and the vibrational mode intensities (Figure 15(d)). This work reported the first *in situ* experimental demonstration of a robust correlation between metal-molecule interactions and the SERS intensity.

Hybridized electric-optical characterization of single-molecule junctions provides a novel technique for investigating EM and CM mechanisms. As the energy levels of singlemolecule junctions can be manipulated by the gate voltage, the study of CM mechanisms can potentially reveal the configurations of single-molecule transistors.

4.3.3 Chemical reactions in single-molecule junctions

The structures of nanoscale metal electrodes are ideal plasmonic structures for SERS analyses. The hot carriers generated from surface plasmons are widely used to catalyze reactions in photocatalytic devices [101], and can be conducted into circuits under an applied bias [102]. For instance, when hot carries generated at the surface of an irradiated Au electrode were injected into molecular or metallic junctions under applied bias, the junction conductance was enhanced [103,104]. The Raman signal is sensitive to electron transfer in single-molecule junctions because the redox states vary in the target molecule. Therefore, hybridized electrical-optical techniques can monitor the transition process of the hot electrons in molecular junctions, which is essential for understanding their photochemistry and for hot-electron manipulation of optoelectronic devices. Monitoring the redox chemistry process caused by SPR-produced hot electrons at the single-molecule scale has attracted great interest [105– 107].

To explore the redox chemistry aroused by the generation and transport of hot electrons, de Nijs *et al.* [108] tracked the Raman spectral evolution of molecular tunneling junctions (MTJs) with a gold nanoparticle-on-mirror (NPoM) geometry (Figure 16(a)). The SAM in their devices provided a pathway for hot-carrier transport. The Raman spectra were dominated by a few molecular junctions within the NPoM hotspot, which was localized in an extremely confined space at the gold particle-molecule-substrate interface. The hot carriers were generated in the gap under irradiation by a 633nm laser. Their transport through the MTJs caused oxidation or reduction of the SAM junctions. To understand the influence of the electron-transfer mechanism, the time-evolved Raman spectra were examined for different types of MTJs dominated by coherent tunneling or hopping mechanisms (Figure 16(b)). The main peak fluctuated dramatically in the hopping-dominated MTJs, whereas the vibrational modes of the coherent tunneling-dominated MTJs were stable (Figure 16(c)). This indicates that the dwell time of the hot electrons was longer in the hopping-dominated MTJs than in the coherent tunneling-dominated MTJs. The fluctuations in the Raman spectra were attributed to the hot electron-induced redox reactions in the MTJs. The residence times of the different Raman shifts reflected the stabilities of the redox states in the MTJs. Methyl-viologen (MV) fixed in a cucurbit [8]uril (CB[8]) molecule exhibited more stable redox states than the other molecules. Therefore, MV was chosen for a molecular-scale study of the redox behavior. By combining bulk experiments with DFT calculations, de Nijs et al. confirmed the fluctuation range of each redox state. Fluctuations in Raman shifts symbolize the behaviors of single molecules, which are determined by their charge states and orientations. In further analyses of the fluctuating Raman shifts, de Nijs et al. [108] obtained the redox dynamics of single MV molecules. The strong correlation between Raman shifts and redox states is significant for monitoring chemical behavior at the single-molecule scale, as demonstrated in Figure 16(d).

As the dwell time in molecular junctions is related to the electron-transfer mechanism, molecular junctions provide a potential reservoir for hot electrons. Hot electrons can modulate the conductance of molecular junctions, and studying the hot electron photochemistry in single-molecule junctions might provide new insights into SPR-induced catalysis.



Figure 16 (a) Diagram of NPoM geometry; (b) structures of six different molecular tunneling junctions (MTJs); (c) time-dependent SERS spectra of MTJs **I–VI**; (d) vibrational peak positions of several NPoMs compared to the three redox states of MV. Reproduced with permission from Ref. [108], copyright 2017, Nature Publishing Group (color online).

Using an MCBJ-SERS method, Zheng et al. [109] probed the dimerization in single-molecule benzene-1,4-dithiol (BDT) junctions (Figure 17(a)). The high- and low-conductance features of the BDT molecular junctions were detected in conductance measurements. The plateau lengths in the two conductance features were distinctly different, being 0.89 nm in the high-conductance state and 1.22 nm in the low-conductance state. The former was consistent with the effective conductive length of single-molecule BDT junctions calculated by DFT. However, the latter plateau was longer than the single-molecule BDT junctions, and the lowand high-conductance states appeared simultaneously in most of the recorded conductance-distance traces. Hence, the low-conductance state was hypothesized to originate from a dimeric BDT junction. Figure 17(b) depicts the hypothesized configuration of the BDT and the dimeric BDT junctions. Corroborating this view, the length of the low-conductance state was consistent with the effective conductive length of the dimeric BDT junction (1.32 nm, calculated by DFT). To further verify their hypothesis, they detected the SERS signals of dimeric BDT junctions in in situ MCBJ-SERS experiments. The spectra are shown in Figure 17(c). The distinct peak at 485 cm⁻¹ was assigned to the vibrational mode of the S-S bond, indicating the formation of dimeric BDT junctions. After breaking the S-S bonds by adding tris (2-carboxyethyl)phosphine hydrochloride (TCEP) to the BDT solution, the electrical signal of the low-conductance state and the Raman signal of the S-S bond disappeared, strongly supporting the hypothesis. The conductance histogram of this control experiment is shown in Figure 17(d). In contrast to previous work on BDT discrepancies, Zheng et al. demonstrated that the low-conductance feature of BDT



Figure 17 (a) Schematic of MCBJ-SERS setup; (b) hypothesized configurations of the high- and low-conductance states; (c) SERS spectra collected during breaking of the junction, and the ordinary spectra of BDT powder; (d) conductance histograms of BDT before (blue) and after (red) TCEP addition. Reproduced with permission from Ref. [109], copyright 2018, Royal Society of Chemistry (color online).

molecular junctions originates from dimeric BDT at the junction. Therefore, hybridized techniques can potentially detect the chemical reactions in single-molecule junctions.

A single-molecule junction is a simple model for investigating chemical mechanisms. However, the experiments are difficult to perform in ambient environments. Analyzing the information in single-molecule data is also difficult, because the conductance and Raman signals of single-molecular junctions are complicated. Future analysis of huge single-molecule data will rely on machine learning techniques.

5 Conclusions and perspective

Owing to advanced syntheses of novel molecular photoswitches for light-modulated molecular devices, and the manipulation of electrical and optical fields, we can now incorporate electroluminescence in biased molecular junctions and characterize the current-carrying junctions. This emerging field still faces many challenges in bridging the electrical and optical properties. Plasmons, which are produced by light-induced electron-hole separation, are the carriers of electron-to-photon or photon-to-electron conversion. Surface plasmon resonance builds a bridge between the electric and optical fields. Unfortunately, the low efficiency of electron-photon conversion limits the performance of single-molecule optoelectronic devices. When designing single-molecule optoelectronic devices, one must consider the configuration of the highly enhanced electromagnetic field and the properties of the molecular junctions. Novel, stable molecular photoswitches with high on/off ratios have not yet been designed, and the mechanisms of light-enhanced quantum transport need better clarification.

Raman spectroscopy is the most powerful technique for obtaining *in situ* information of single-molecule junctions. Nevertheless, distinguishing the meaningful signals from the statistical conductance data and the Raman spectra of the dynamics of single-molecule junctions is challenged by the uncertainties in single-molecule events. Controlling the probabilities of specific events by external stimulation and combining the observations with theoretical calculations might improve our interpretations of complex data. Theories and calculation tools also require further development [110–113].

Monitoring chemical reactions and dynamics at the singlemolecule scale has aroused much concerns [87,114]. We foresee that hybridized electrical-optical techniques such as MCBJ-SERS and STMBJ-TERS will become powerful tools for investigating the chemical reactions and dynamics of single-molecule junctions. Operating and characterizing the light-molecule interactions in single-molecule junctions will improve our fundamental understanding and inspire new applications of single-molecule optoelectronics.

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